

AMENDED SPECIFICATION

Reprinted as amended in accordance with the decision of the Superintending Examiner acting for the Comptroller-General, dated the seventh day of July, 1959, under Section 14, of the Patents Act, 1949.

PATENT SPECIFICATION

DRAWINGS ATTACHED

789,228



Date of Application and filing Complete Specification: Nov. 29, 1954.

No. 34493/54.

Application made in Netherlands on Nov. 30, 1955.

Complete Specification Published: Jan. 15, 1958.

Index at acceptance:—Classes 2(3), B1H; and 32, E2.

International Classification:—C10g.

COMPLETE SPECIFICATION

Improvements in or relating to Thermal Cracking Processes and Plant therefor

ERRATA

AMENDED SPECIFICATION NO. 789,228

Page 1, in the heading, for "Application made in Netherlands on Nov. 30, 1955." read "Application made in Netherlands on Nov. 30, 1953."

Page 4, line 113, for "high" read "higher".

THE PATENT OFFICE,
19th January, 1960

DB 29787/1(11)/3920 200 1/60 R

Thus, products consisting chiefly of liquid alkenes may be obtained by the vapour phase cracking, at for example 550° C. to 560° C., of high molecular weight hydrocarbon oils boiling below approximately 450° C. When higher cracking temperatures, e.g. 700° C. to 800° C., are employed considerable quantities of lower gaseous alkenes, including ethene, are produced by thermally cracking high-boiling hydrocarbon oils.

Hitherto, hydrocarbon starting materials boiling above 450° C., such as the residues obtained in the distillation of petroleum or petroleum products, have not been suitable for use on a technical scale, owing to the risk of the cracking equipment becoming clogged by carbonaceous deposits and the fact that such higher boiling materials cannot be vaporised sufficiently rapidly in conventional cracking plant that no cracking occurs before the initial [Price 3s. 6d.]

chiefly normal paraffins, is that the starting material has to be raised very rapidly to cracking temperature in order to prevent undesirable changes therein. When high temperature gradients are employed for this purpose there is a risk of the starting material becoming overheated, with the result that undesirable changes, such as a structural modification of the hydrocarbon molecule (for instance a skeleton isomerisation in the case of normal paraffins) occur. Such isomerisations increase with the temperature at which vaporization of the initial material is carried out: consequently they occur to a greater extent when using high-boiling initial materials.

It has now been found that paraffin-containing mixtures of higher hydrocarbons containing not more than 25% by weight of aromatic hydrocarbons can be made to give high yields of ethene or a product consisting chiefly of liquid alkenes, depending on the

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COMPLETE SPECIFICATION

Improvements in or relating to Thermal Cracking Processes and Plant therefor

We, NAAMLooZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of The Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the preparation of ethene or products consisting mainly of liquid alkenes by the thermal cracking of higher hydrocarbons.

Alkenes may be prepared by thermally cracking high boiling hydrocarbons or hydrocarbon mixtures containing high boiling components. Thus, products consisting chiefly of liquid alkenes may be obtained by the vapour phase cracking, at for example 550° C. to 560° C., of high molecular weight hydrocarbon oils boiling below approximately 450° C. When higher cracking temperatures, e.g. 700° C. to 800° C., are employed considerable quantities of lower gaseous alkenes, including ethene, are produced by thermally cracking high-boiling hydrocarbon oils.

Hitherto, hydrocarbon starting materials boiling above 450° C., such as the residues obtained in the distillation of petroleum or petroleum products, have not been suitable for use on a technical scale, owing to the risk of the cracking equipment becoming clogged by carbonaceous deposits and the fact that such higher boiling materials cannot be vaporised sufficiently rapidly in conventional cracking plant that no cracking occurs before the initial

material is completely vaporised. Such premature cracking adversely affects the quality of the liquid alkenes produced.

In prior cracking processes the heat required to raise the initial material to cracking temperature is usually supplied indirectly, involving heat transfer through a wall. Exceptionally heavy demands are made on the material of the wall through which the heat-transmission takes place, particularly when high cracking temperatures, such as 600° C. or more, are employed. This necessitates the use of expensive materials of construction, such as special types of steel. Another drawback, especially when high yields of unbranched alkenes are required from initial materials comprising chiefly normal paraffins, is that the starting material has to be raised very rapidly to cracking temperature in order to prevent undesirable changes therein. When high temperature gradients are employed for this purpose there is a risk of the starting material becoming overheated, with the result that undesirable changes, such as a structural modification of the hydrocarbon molecule (for instance a skeleton isomerisation in the case of normal paraffins) occur. Such isomerisations increase with the temperature at which vaporization of the initial material is carried out: consequently they occur to a greater extent when using high-boiling initial materials.

It has now been found that paraffin-containing mixtures of higher hydrocarbons containing not more than 25% by weight of aromatic hydrocarbons can be made to give high yields of ethene or a product consisting chiefly of liquid alkenes, depending on the

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cracking temperature employed, by a continuous thermal cracking process of the kind which comprises passing the paraffin-containing hydrocarbon mixture upwardly through a tubular reaction zone in contact with a hot, finely-divided, solid, inert heat-transfer agent which is in the form of a dilute suspension in a gaseous fluidising agent at such a rate that the contact time in said reaction zone is less than 2 seconds, separating the resulting cracked product vapours and the heat-transfer agent, heating said heat-transfer agent in a separate heating zone and recycling the heated heat-transfer agent to said reaction zone, the reaction and heating zones being provided with risers and the fluidized solid being fed from one zone to the other via auxiliary chambers surrounding the lower parts of the risers and communicating therewith through openings in the wall of the risers, the rate at which the heat transfer agent enters the said risers being regulated by injection of steam into said auxiliary chambers.

The heat-transfer agent should be heated to such a high temperature that the hydrocarbon material to which it transfers heat by direct contact therewith is raised to the desired cracking temperature in the reaction zone. This cracking temperature is at least approximately 700° C. when mainly ethene is to be produced and between approximately 550 and 650° C. when mainly liquid alkenes are required.

The starting material to be cracked is advantageously preheated. Thus, if this material is not liquid owing to the presence therein of normally solid paraffins, it should be sufficiently pre-heated to liquefy it. The starting material, which is fed into the reaction zone in liquid form, immediately evaporates on contact with the hot heat-transfer agent. If the starting material can be vaporised without danger of liquid phase cracking, it can, if desired, be so vaporised before contacting it with the hot heat-transfer agent.

It has been found of vital importance so to regulate the flow rate through the reaction zone of the paraffin-containing hydrocarbon material to be cracked that this material remains in contact with the hot heat-transfer agent for a period not exceeding 2 seconds. The contact times with which optimum results are obtained vary, within this specified period, in accordance with the cracking temperature employed; in general they decrease as the latter increases. For the manufacture of ethene, for which cracking temperatures of at least 700° C., preferably between approximately 750° C. and 850° C., are employed, the contact times are preferably between approximately 0.1 and 1 second, whereas for the manufacture of mainly liquid alkenes which takes place at lower temperatures, for example between approximately 550° C. and 650° C., somewhat longer contact periods of between approximately 0.5 and 1.5 seconds, are to be preferred.

In order as far as possible to avoid undesirable further contact of the hydrocarbon vapours with the hot finely-divided heat-transfer agent, care should be taken to separate the hydrocarbon vapours from the heat-transfer agent or at least the bulk thereof as quickly as possible after the hydrocarbon-containing mixture leaves the reaction zone. Having regard to the upward direction in which the hydrocarbon reactant and the heat-transfer agent are led through the reaction zone, the rapid separation required can be readily effected, for example by disposing a baffle just above the reaction zone.

In carrying out the process of the present invention the circulation of the heat-transfer agent through the reaction zone and the separate heating zone is advantageously effected by circulating the finely-divided heat-transfer agent in a fluidised state in which it is maintained by the introduction of a gaseous or vaporous medium.

Suitable starting materials comprise any mixtures of higher hydrocarbons containing paraffin hydrocarbons, of natural or synthetic origin and preferably containing little or no aromatics, and in any case, less than 25%, by weight, of aromatics. Examples of suitable initial materials are paraffin-containing mineral oil distillates or carbon monoxide hydrogenation products or other material rich in paraffins, such as the paraffin wax obtained when dewaxing lubricating oils. Paraffin-containing raffinates containing less than 25% by weight of aromatics obtained by the extraction with selective solvents, e.g. furfural, of the heavy cycle oil, obtained in the catalytic cracking of hydrocarbon oils are also suitable initial materials.

In particular, hydrocarbon mixtures, such as paraffin-containing residues boiling above 450° C. and obtained when distilling mineral oils or mineral oil products, which are unsuitable for processing on a technical scale by conventional vapour phase cracking processes, may be treated satisfactorily by the process of the present invention.

Any finely-divided, i.e. powdery or granular, solid substance, for example sand, alumina and ground pumice-stone, which is inert and heat-resistant, may be used as the heat transfer agent in the process in accordance with the present invention.

The desired rate of flow of the hydrocarbon material and the hot finely-divided solid heat-transfer agent through the reaction zone is preferably regulated by the injection of steam as the fluidizing agent into the lower part of the reaction zone and the desired rate of flow through the heating zone in which the heat-transfer agent is re-heated to the required temperature may be effected by the use of hot combustion gases, which at the same time raise the heat-transfer agent to the required temperature.

In carrying out the process of the invention

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the heat-transfer agent, which circulates in a fluidised state from the heating zone to the reaction zone and then from the reaction zone back to the heating zone, is passed via auxiliary chambers provided round the lower parts of the reaction zone and the heating zone and communicating with the reaction zone and the heating zone respectively, the heat-transfer agent being maintained in a fluidised state in these auxiliary chambers by the injection of steam therein. The amount of heat-transfer agent fed into the reaction zone and into the heating zone, from the respective auxiliary chambers, can be effectively controlled, without the need of regulating valves, by controlling the amount of steam introduced as the fluidising medium.

After most of the heat-transfer agent has been separated from the vaporous reaction mixture leaving the reaction zone, it is advisable to cool the reaction product rapidly to well below the cracking temperature, for example to between 350° C. and 450° C., in order to prevent further cracking which may lead to undesirable coke formation. This rapid decrease in temperature can be achieved effectively by quenching the hot vapours by bringing them into direct contact with a non-reactive, liquid or vaporous medium of a considerably lower temperature, e.g. cold water which is injected into the vaporous reaction product by means of nozzles.

When operating under optimal conditions for the formation of ethene, i.e. at cracking temperatures in the reaction zone of from 700° C. to 900° C. and with contact times of from approximately 0.1 to 1 second, good yields of ethene, e.g. 25% to 30% or more, are obtained by the process of the present invention. In addition to ethene, other normally gaseous hydrocarbons, including alkenes such as propene and butenes, and also hydrocarbon mixtures, liquid at normal temperature and rich in aromatics, from which can be separated gasoline fractions and higher boiling fractions suitable as motor fuel or a component thereof, are produced.

The process of the invention may also be carried out in such a manner that the cracking results mainly in the production of hydrocarbon mixtures which are liquid at ordinary temperatures, such mixtures consisting mainly of liquid alkenes, with relatively small quantities of ethene and other gaseous alkenes as by-products. Preferably, when the process of the present invention is carried out in this way, the temperatures in the reaction zone should be between 550 and 650° C. with contact times of from 0.5 to 1.5 seconds. With starting materials containing more than 40% of paraffins (and less than 25% of aromatics), high yields of the higher alkenes having eight and more carbon atoms per molecule are obtained. These alkenes are predominantly unbranched and are especially suitable for the

preparation of surface-active, secondary sulphuric acid alkyl ester salts of excellent quality. In this way high-boiling materials, e.g. paraffin wax containing more than 10% of components boiling above 470° C., can be converted into good quality higher alkenes for the preparation of sulphuric acid ester salts.

If, in carrying out the process of the present invention, small quantities of carbonaceous material deposit on the solid particles of the hot heat-transfer agent whilst it is in contact with the hydrocarbons in the reaction zone, this carbonaceous material is wholly or mainly burnt off whilst the heat-transfer agent is being re-heated in the heating zone.

The present invention will now be further described with reference to the accompanying drawing which shows diagrammatically a cracking plant for thermally cracking high-boiling hydrocarbons to produce mainly ethene or alternatively, depending on process conditions, mainly liquid products consisting chiefly of higher alkenes.

The cracking plant includes a reactor 1 in which cracking takes place, and a heater 7 in which the heat transfer agent is heated to the required temperature. The reactor 1 is provided with a riser 2 and is connected via a line 3 with a cyclone 4 provided with a discharge line 5 and a recycle line 6. The heater 7 is also provided with a riser 8 at the bottom of which is a burner 9, and it is connected via a discharge line 10 to a separator 11 having a recycle line 12 and a connection at its upper end to a chimney 13 through a regulating valve 14. The reactor 1 and the heater 7 are interconnected by means of a line 15 leading to the reactor 1 from an auxiliary chamber 16 surrounding the lower part of the riser 8 and in communication therewith through openings 17. The reactor 1 and the heater 7 are also interconnected by means of a line 18 leading from the heater 7 to an auxiliary chamber 19 provided round the lower part of the riser 2 and in communication therewith through openings 20.

Fuel fed through a line 21 is burned in the burner 9 with air fed under pressure through a line 22. Sand or another inert, finely-divided heat-transfer agent is fed at such a rate from the auxiliary chamber 16 via the openings 17 into the combustion gases flowing upward through the riser 8 that it becomes heated to the required temperature by contact with the hot combustion gases. When preparing ethene, this temperature is, for example, approximately 800° C. Most of the hot heat-transfer agent is separated from the combustion gases by means of a baffle plate 23 disposed above the riser 8, the solid particles falling into the fluidised bed maintained at the bottom of the heater 7 by means of steam admitted through an annular distributor 24. The combustion gases discharged from the heater 7 through the line 10 pass through a separator 11 to the chimney 13

13. In the separator 11 any solid particles remaining in the combustion gases are separated and led back through a line 12 to the fluidised bed maintained at the bottom of the heater 7.

5 The hot heat-transfer agent flows in a fluidised state from the heater 7 through the line 18 to the auxiliary chamber 19 below the reactor 1, whence it enters the lower part of the riser 2 through the openings 20. The hot particles are carried up the riser 2 by means of steam fed thereto through a line 25. The hydrocarbon material to be cracked is fed, in a pre-heated state, through a line 26 into the riser 2 in which it immediately evaporates on contacting the ascending hot particles of the heat-transfer agent and is very rapidly raised to the cracking temperature, e.g. 700° C. for the preparation of ethene. Most of the solid particles of heat-transfer agent are separated from the mixture of gases and solid particles leaving the top of riser 2, by means of a baffle 27, the separated particles then falling into a fluidised bed thereof which is maintained in the lower part of the reactor 1 by means of steam introduced through an annular distributor 28. The flow rate through the cracking zone is so regulated that the hydrocarbon material is kept at the cracking temperature for only a very short time (e.g. less than 1 second for ethene preparation) by contact with the heat-transfer agent for a period not exceeding 2 seconds.

35 The gaseous reaction products rising in the reactor 1 are rapidly cooled to below cracking temperature, e.g. to 450° C., by water injected through nozzles 29. The cooled gases then flow via the line 3 to cyclone 4 in which any solid particles entrained therein are separated and recycled via line 6 to the fluidised bed at the bottom of the reactor 1, while the gases flow out of the cyclone via a discharge line 5 to a product recovery plant (not shown).

45 The solid particles which are still hot are recycled continuously from the fluidised bed at the bottom of the reactor 1 via the line 15 to the auxiliary chamber 16, from which they are fed into the riser 8 to be re-heated therein to the desired temperature by contact with combustion gases from the burner 9.

50 The steam introduced via the annular distributors 24 and 28 serves to not only maintain the finely-divided heat-transfer agent in the heater 7 and the reactor 1 in a fluidised state, but also as a stripping agent for preventing combustion gases from entering riser 2 from the heater 7, and also for preventing the reaction products from entering the riser 8 from the reactor 1.

60 Steam is also injected into the auxiliary chambers 16 and 19 through distributors 30 and 31 in order to keep the heat-transfer agent therein in a fluidised state. By regulating the supply of steam through these distributors 30, 31 the rate at which the heat-transfer agent enters the risers 8 and 2 can be simply and

effectively regulated.

The cracking plant required for carrying out the process of the invention may be made for the greater part of relatively cheap materials of construction, such as ordinary steel. Also, most of the parts thereof may be insulated on the inside in order to keep the wall temperatures and heat losses as low as possible. The inside of the cyclone 4 would not be insulated in view of the risk of such an insulation becoming rapidly affected by erosion: it may, however, be made of a steel alloy able to withstand high temperatures and erosion. The risers 2 and 8 may also be made of such an alloy steel.

The cracking process of the present invention is illustrated by the following example:—

EXAMPLE.

By means of the cracking plant described above, a paraffinous oil residue boiling above 500° C. and containing less than 25% by weight of aromatics was thermally cracked, using sand as the heat-transfer agent. The sand was heated to approximately 800° C. in the heater 7. The feed rates of the oil residue, which was pre-heated to approximately 100° C., and of the hot sand in the riser 2 were so adjusted that the temperature of the mixture of sand and vapour issuing from the top of the riser 2 was approximately 700° C. and the contact time in the reaction zone was approximately 0.4 second. The vaporous mixture discharged from the cyclone 4 contained 70% of components boiling below 30° C.: the amount of such components was approximately 60% by weight of the starting material.

From that part of the product boiling below 30° C. in ethene-ethane fraction containing approximately 90% ethene, was obtained by fractional distillation and amounted to approximately 30% by weight of the starting material. In addition a propene fraction and a butene fraction amounting to approximately 15 and 13% by weight, respectively, of the starting material were also obtained.

WHAT WE CLAIM IS:—

1. A continuous process for thermally cracking a paraffin-containing mixture of high hydrocarbons containing not more than 25% by weight of aromatic hydrocarbons, in which the paraffin containing hydrocarbon mixture is passed upwardly through a tubular reaction zone in contact with a hot, finely divided, solid, inert heat-transfer agent which is in the form of a dilute suspension in a gaseous fluidizing agent, at such a rate that the contact time in said reaction zone is less than 2 seconds, separating the resulting cracked product vapours and the heat-transfer agent, heating said heat-transfer agent in a separate heating zone and recycling the heated heat-transfer agent to the said reaction zone, the reaction and heating zones being provided with risers and the fluidized solid being fed from one zone to the other via auxiliary chambers surrounding

- the lower parts of the risers and communicating therewith through openings in the wall of the risers, the rate at which the heat transfer agent enters the said risers being regulated by injection of steam into said auxiliary chambers.
2. A process as claimed in claim 1, wherein the mixture of higher hydrocarbons is a paraffin-containing residue boiling above 450° C., and obtained by distilling mineral oils or mineral oil products.
3. A process as claimed in either of the preceding claims, wherein the mixture of higher hydrocarbons is heated in the reaction zone to a temperature of at least 700° C.
4. A process as claimed in claim 3, wherein the mixture of higher hydrocarbons is heated in the reaction zone to between 750° C. and 850° C.
5. A process as claimed in claim 3 or claim 4, wherein the contact time is between approximately 0.1 and 1 second.
6. A process as claimed in claim 1 or claim 2, wherein the mixture of higher hydrocarbons is heated in the reaction zone to a temperature between approximately 550° C. and 650° C.
7. A process as claimed in claim 6, wherein the contact time is between approximately 0.5 and 1.5 seconds.
8. A process as claimed in any one of the preceding claims, wherein the heat-transfer agent is circulated from said reaction zone, through the heating zone and back to said reaction zone in a fluidised state.
9. A process as claimed in any one of the preceding claims, wherein the flow rate through said reaction zone is regulated by injecting steam as the fluidising agent into the lower part of the reaction zone, and wherein the rate of flow of said heat-transfer agent through the heating zone is regulated by injecting hot combustion gases into the lower part of said heating zone.
10. A process as claimed in any one of the preceding claims, wherein a rapid separation between the hydrocarbon vapours and the heat-transfer agent leaving said reaction zone is effected with the aid of a baffle disposed above the reaction zone.
11. A process as claimed in any one of the preceding claims, wherein the hydrocarbon vapours, after separation from the heat-transfer agent, are contacted with a liquid or vaporious medium whose temperature is considerably lower than that of said hydrocarbon vapours.
12. A continuous thermal cracking process for preparing ethene or a reaction product consisting chiefly of liquid alkenes substantially as hereinbefore described.
13. Alkenes when prepared by the process claimed in any one of the preceding claims.
14. A cracking plant for carrying out the process claimed in any one of claims 1—12 substantially as hereinbefore described and as shown diagrammatically in the accompanying drawing.

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